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STANDARD METHODS

FOR THE EXAMINATION OF WATER AND WASTEWATER

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3500-As ARSENIC*

3500-As A. Introduction

1. Occurrence and Significance

Severe poisoning can arise from the ingestion of as little as 100 mg arsenic trioxide; chronic effects may result from the accumulation of arsenic compounds in the body at low intake levels. Carcinogenic properties also have been imputed to arsenic compounds. The arsenic concentration in most potable waters seldom exceeds 10 μg/L, although values as high as 100 μg/L have been reported. Aqueous arsenic in the form of arsenite, arsenate, and organic arsenicals may result from mineral dissolution, industrial discharges, or the application of herbicides. The chemical form of arsenic depends on its source (inorganic arsenic from minerals, industrial discharges, and insecticides; organic arsenic from industrial discharges, insecticides, and biological action on inorganic arsenic). The toxicity of arsenic depends on its chemical form.

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* Approved by Standard Methods Committee, 1990.

2. Selection of Method

Methods are available to identify and determine arsenite, arsenate, methylarsonic acid, dimethylarsinic acid, arsenocholine, arsenobetaine, and other organic arsenic compounds. Unpolluted fresh water normally does not contain organic arsenic compounds, but may contain inorganic arsenic compounds in the form of arsenate and arsenite. The hydride generation-atomic absorption method (B), which converts arsenic compounds to their hydrides that subsequently are decomposed in an argon-hydrogen flame, is the method of choice, although the electrothermal method (direct injection of sample into the graphite tube) is simpler in the demonstrated absence of interferences. The silver diethyldithiocarbamate method (C), in which arsine is generated by sodium borohydride in acidic solution, is applicable to the determination of total inorganic arsenic when interferences are absent and the sample contains no methylarsenic compounds. Because arsenite is more toxic than arsenate, a method for identification of these two species and quantification is needed and is available in the diethyldithiocarbamate method (C). The inductively coupled plasma (ICP) method (D) is useful at higher concentrations (greater than 50 µg/L).

3500-As B. Atomic Absorption Spectrometric Method

See electrothermal atomic absorption spectrometric method, Section 3113, and hydride generation atomic absorption spectrometric method, Section 3114.

3500-As C. Silver Diethyldithiocarbamate Method

1. General Discussion

a. Principle: Arsenite, containing trivalent arsenic, is reduced selectively by aqueous sodium borohydride solution to arsine, AsH_3, in an aqueous medium of pH 6. Arsenate, methylarsonic acid, and dimethylarsenic acid are not reduced under these conditions. The generated arsine is swept by a stream of oxygen-free nitrogen from the reduction vessel through a scrubber containing glass wool or cotton impregnated with lead acetate solution into an absorber tube containing silver diethyldithiocarbamate and morpholine dissolved in chloroform. A red color develops, the intensity of which is measured at 520 nm. To determine total inorganic arsenic in the absence of methylarsenic compounds, reduce another sample portion at a pH about 1. Alternatively, determine arsenate in a sample from which arsenite has been removed by reduction at pH 6, after acidification with hydrochloric acid and addition of another portion of sodium borohydride solution. Collect the arsine formed from arsenate in fresh absorber solution.

b. Interferences: Although certain metals—chromium, cobalt, copper, mercury, molybdenum, nickel, platinum, silver, and selenium—influence the generation of arsine, their concentrations in water seldom are high enough to interfere. H_2S interferes, but the interference is removed with lead acetate. Antimony is reduced to stibine, which forms a colored complex with an absorption maximum at 510 nm and interferes with the arsenic determination. Methylarsenic compounds are reduced at pH 1 to methylarsines, which form colored complexes with the absorber solution. If methylarsenic compounds are present, measurements of total arsenic and arsenate are unreliable. The results for arsenite are not influenced by methylarsenic compounds.

c. Minimum detectable quantity: 1 µg arsenic.

2. Apparatus

a. Arsine generator, scrubber, and absorption tube: See Figure 3500-As:1. Use a 200-mL three-necked flask with a sidearm (19/22 or similar size female ground-glass joint) through which the inert gas delivery tube reaching almost to the bottom of the flask is inserted; a 24/40 female ground-glass joint to carry the scrubber; and a second side arm closed with a rubber septum, or preferably by a screw cap with a hole in its top for insertion of a TFE-faced silicon septum. Place a small magnetic stirring bar in the flask. Fit absorber tube (20 mL capacity) to the scrubber and fill with silver diethyldithiocarbamate solution. Do not use rubber or cork stoppers because they may absorb arsine. Clean glass equipment with concentrated nitric acid.

b. Fume hood: Use apparatus in a well-ventilated hood with flask secured on top of a magnetic stirrer.

c. Photometric equipment:

1) *Spectrophotometer,* for use at 520 nm.

2) *Filter photometer,* with green filter having a maximum transmittance in the 500- to 540-nm range.

3) *Cells,* for spectrophotometer or filter photometer, 1-cm, clean, dry, and each equipped with a tightly fitting cover (TFE stopper) to prevent chloroform evaporation.

3. Reagents

a. Distilled/deionized water.

b. Acetate buffer, pH 5.5: Mix 428 mL 0.2*M* sodium acetate, $NaC_2H_3O_2$, and 72 mL 0.2*M* acetic acid, CH_3COOH.

c. Sodium acetate, 0.2*M*: Dissolve 16.46 g anhydrous sodium acetate or 27.36 g sodium acetate trihydrate, $NaC_2H_3O_2 \cdot 3H_2O$, in water. Dilute to 1000 mL with water.

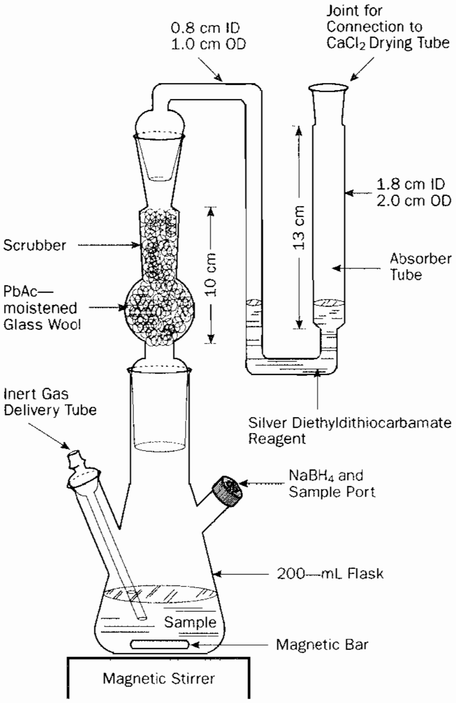

Figure 3500-As:1. Arsine generator and absorber assembly.

d. Acetic acid, 0.2*M*: Dissolve 11.5 mL glacial acetic acid in water. Dilute to 1000 mL.

e. Sodium borohydride solution, 1%: Dissolve 0.4 g sodium hydroxide, NaOH (4 pellets), in 400 mL water. Add 4.0 g sodium borohydride, $NaBH_4$ (check for absence of arsenic). Shake to dissolve and to mix. Prepare fresh every few days.

f. Hydrochloric acid, HCl, 2*M*: Dilute 165 mL conc HCl to 1000 mL with water.

g. Lead acetate solution: Dissolve 10.0 g $Pb(CH_3COO)_2 \cdot 3H_2O$ in 100 mL water.

h. Silver diethyldithiocarbamate solution: Dissolve 1.0 mL morpholine (CAUTION: *Corrosive—avoid contact with skin*) in 70 mL chloroform, $CHCl_3$. Add 0.30 g silver diethyldithiocarbamate, $AgSCSN(C_2H_5)_2$; shake in a stoppered flask until most is dissolved. Dilute to 100 mL with chloroform. Filter and store in a tightly closed brown bottle in a refrigerator.

i. Stock arsenite solution: Dissolve 0.1734 g $NaAsO_2$ in water and dilute to 1000 mL with water; 1.00 mL = 100 μg As. CAUTION: *Toxic—avoid contact with skin and do not ingest.*

j. Intermediate arsenite solution: Dilute 10.0 mL stock solution to 100 mL with water; 1.00 mL = 10.0 μg As.

k. Standard arsenite solution: Dilute 10.0 mL intermediate solution to 100 mL with water; 1.00 mL = 1.00 μg As.

l. Standard arsenate solution: Dissolve 0.416 g $Na_2HAsO_4 \cdot 7H_2O$ in water and dilute to 1000 mL. Dilute 10.0 mL to 100 mL with water; dilute 10 mL of this intermediate solution to 100 mL; 1.00 mL = 1.00 μg As.

4. Procedure

a. Arsenite:

1) Preparation of scrubber and absorber—Dip glass wool into lead acetate solution; remove excess by squeezing glass wool. Press glass wool between pieces of filter paper, then fluff it. Alternatively, if cotton is used treat it similarly but dry in a desiccator and fluff thoroughly when dry. Place a plug of loose glass wool or cotton in scrubber tube. Add 4.00 mL silver diethyldithiocarbamate solution to absorber tube (5.00 mL may be used to provide enough volume to rinse spectrophotometer cell).

2) Loading of arsine generator—Pipet not more than 70 mL sample containing not more than 20.0 μg As (arsenite) into the generator flask. Add 10 mL acetate buffer. If necessary, adjust total volume of liquid to 80 mL. Flush flask with nitrogen at the rate of 60 mL/min.

3) Arsine generation and measurement—While nitrogen is passing through the system, use a 30-mL syringe to inject through the septum 15 mL 1% sodium borohydride solution within 2 min. Stir vigorously with magnetic stirrer. Pass nitrogen through system for an additional 15 min to flush arsine into absorber solution. Pour absorber solution into a clean and dry spectrophotometric cell and measure absorbance at 520 nm against chloroform. Determine concentration from a calibration curve obtained with arsenite standards. If arsenate also is to be determined in the same sample portion save liquid in the generator flask.

4) Preparation of standard curves—Treat standard arsenite solution containing 0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 μg As described in ¶s 1) through 3) above. Plot absorbance versus micrograms arsenic in the standard.

b. Arsenate: After removal of arsenite as arsine, treat sample to convert arsenate to arsine:

If the lead acetate-impregnated glass wool has become ineffective in removing hydrogen sulfide (if it has become gray to black) replace glass wool [see ¶ 4*a*1)]. Pass nitrogen through system at the rate of 60 mL/min. Cautiously add 10 mL 2.0*N* HCl. Generate arsine as directed in ¶ 4*a*3) and prepare standard curves with standard solutions of arsenate according to procedure of ¶ 4*a*4).

c. Total inorganic arsenic: Prepare scrubber and absorber as directed in ¶ 4*a*1) and load arsine generator as directed in ¶ 4*a*2) using 10 mL 2.0*N* HCl instead of acetate buffer. Generate arsine and measure as directed in ¶ 4*a*3). Prepare standard curves according to ¶ 4*a*4). Curves obtained with standard arsenite are almost identical to those obtained with arsenate standard solutions. Therefore, use either arsenite or arsenate standards.

5. Calculation

Calculate arsenite, arsenate, and total inorganic arsenic from readings and calibration curves obtained in 4*a*, *b*, and *c*, respectively, as follows:

$$\text{mg As/L} = \frac{\mu\text{g As (from calibration curve)}}{\text{mL sample in generator flask}}$$

6. Precision and Bias

Interlaboratory comparisons have not been made yet. The relative standard deviation of results obtained with arsenite/arsenate mixtures containing approximately 10 μg arsenic were less than 10%.

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3500-As D. Inductively Coupled Plasma Method

See Section 3120.

3500-Ba BARIUM*

3500-Ba A. Introduction

1. Occurrence and Significance

Barium stimulates the heart muscle. However, a barium dose of 550 to 600 mg is considered fatal to human beings. Afflictions arising from its consumption, inhalation, or absorption involve the heart, blood vessels, and nerves.

Despite a relative abundance in nature (16th in order of rank), barium occurs only in trace amounts in water. The barium concentration of U.S. drinking waters ranges between 0.7 and 900 μg/L, with a mean of 49 μg/L. Higher concentrations in drinking water often signal undesirable industrial waste pollution.

2. Selection of Method

Perform analyses by the atomic absorption spectrometric method or the inductively coupled plasma method.

3500-Ba B. Atomic Absorption Spectrometric Method

See flame atomic absorption spectrometric method, Section 3111D, and electrothermal atomic absorption spectrometric method, Section 3113.

3500-Ba C. Inductively Coupled Plasma Method

See Section 3120.

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*Approved by Standard Methods Committee, 1990.